Rev.Adv.Mater.Sci. 6 (2004) 41-47

DIFFUSION PERCOLATION ALONG TRIPLE JUNCTIONS IN NANOCRYSTALLINE MATERIALS

I.A. Ovid'ko and A.G. Sheinerman

Institute of Problems of Mechanical Engineering, Russian Academy of Sciences, Bolshoj 61, Vasil. Ostrov, St. Petersburg 199178, Russia

Received: February 11, 2004

Abstract. A theoretical model is suggested which describes percolation of enhanced diffusion along triple junctions of grain boundaries in nanocrystalline materials with very small grains. The effective diffusion coefficient is defined and calculated which takes into account a distribution of diffusivities among triple junctions that form a network in a nanocrystalline solid. It is shown that the effective diffusion coefficient is lower than the average diffusion coefficient in nanocrystalline materials.

1. INTRODUCTION

The rapidly growing scientific and technological interest in nanocrystalline materials has arisen from the unique properties associated with their nanograined structure; see, e.g., [1-4]. Among the most important issues for the outstanding properties of nanocrystalline materials are the effects of triple junctions of grain boundaries (GBs), whose volume fraction is extremely high in these materials. In recent years, triple junctions of GBs in nano-and polycrystalline materials have been recognized as defects with the structure and properties being essentially different from those of GBs that they adjoin (for a review, see [5]). For instance, from experimental data and theoretical models it follows that triple junctions play the role of enhanced diffusion tubes [6,7], nuclei of the enhanced segregation of the second phase [8,9], strengthening elements and sources of lattice dislocations [10-14] during plastic deformation, carriers of enhanced diffusional creep [15], drag centers of grain boundary migration during re-crystallization processes [16,17] and places for preferable generation of nanoscale cracks [18,19]. With a very high density of triple junctions in nanocrystalline materials, their influence on the behavior of such materials is essential or even crucial.

In particular, the role of triple junctions is expected to be very important in diffusion processes which crucially affect their outstanding mechanical and sensing characteristics of nanocrystalline materials. Following experimental data [8], diffusion along triple junctions of grain boundaries is characterized by the diffusion coefficient D being several orders (three of more) of magnitude larger than the coefficient D_{gb} characterizing diffusion along grain boundary planes. Grain boundary diffusion coefficient D_{gb}, in its turn, is by several orders larger than the bulk diffusion coefficient D_{bulk}; see [20] and references therein. With these experimental data, we expect that the triple junction diffusion crucially contributes to diffusion processes in nanocrystalline materials where the volume fraction of the triple junction phase is very high, that is, materials have the very small grain size $d < 10$ nm. In this paper, we will focus our

Corresponding author: e-mail I.A. Ovid'ko, e-mail: ovidko@def.ipme.ru

consideration on triple junction diffusion as the dominant diffusion channel in nanocrystalline materials with very small grains.

In general, diffusivity along a triple junction is sensitive to its structure, in which case different triple junctions (with different structures) are characterized by different diffusion coefficients. It is supported by experimental data discussed in a review article [5], which are indicative of the fact that different triple junctions often have different properties. In this context, the diffusion behavior of a nanocrystalline specimen with very small grains is expected to depend on the distribution of diffusivities among its triple junctions and geometry of the triple junction ensemble. The main aim of this paper is to suggest a theoretical model describing enhanced diffusion along triple junction networks in nanocrystalline materials with the effect of a diffusivity distribution taken into account.

2. ENHANCED DIFFUSION PERCOLATION ALONG TRIPLE JUNCTIONS. MODEL

Let us estimate the range of the grain size d in which the triple junction diffusion is dominant in a nanocrystalline material. In the first approximation, the contributions of triple junction, grain boundary and bulk diffusion processes to overall diffusion are characterized by products $f D$, $f_{gb} D_{gb}$ and $f_{bulk} D_{bulk}$, respectively. Here f, f_{gb} and f_{bulk} are the volume fractions of the triple junction, grain boundary and grain interior phases, respectively. For characteristic values of $D = 10^3 D_{gb}$ [8] and $D_{gb}=10^3 D_{bulk}$ [20] and estimates [21] of $f >0.02$, $f_{gb}>0.2$ and $f_{bulk}<0.8$ in the grain size range $d<10$ nm, we find that $f D$ is much larger than $f_{gb}D_{gb}$ and $f_{bulk}D_{bulk}$ in this range. At the same time, nanocrystalline bulk materials and coatings with very small grain sizes $d<10$ nm exhibit the outstanding deformation behavior [22-24] with grain boundary and triple junction diffusional creep modes playing an important role; see, e.g., [25]. In this context, it is highly interesting to adequately describe diffusion characteristics in nanocrystalline bulk materials and coatings with very small grains.

As noted in the Introduction, the diffusion behavior of a nanocrystalline specimen with very small grains is expected to depend on the distribution of diffusivities among its triple junctions and geometry of the triple junction ensemble. As a corollary, the macroscopic diffusion coefficient measured in conventional experiments is not simply a mean coefficient. Diffusion is caused by percolation of enhanced diffusion along triple junctions, which is characterized by an effective diffusion coefficient. This coefficient is sensitive to both the diffusivity distribution among triple junctions and geometry of the triple junction ensemble in a nanocrystalline solid. In general, the effective diffusion coefficient is different from the mean diffusion coefficient.

In this paper we will estimate the effective diffusion coefficient in the framework of the following first approximation model. We model the triple junction network as a two-dimensional square lattice whose edges represent triple junctions with different values of the diffusion coefficient. The calculation scheme used in our calculation is independent on dimensions of the system. The two-dimensional model is chosen here for simplicity of calculations, while topology of the square network containing quadruple node points is close to topology of real three-dimensional networks of triple junctions that commonly form quadruple nodes in real nano- and polycrystalline solids. With experimental data on high values of triple junction diffusion compared to bulk and GB diffusion [8], in our first approximation model, we do not examine jumps of atoms from triple junctions to grain interiors and boundaries and vice versa. That is, diffusion processes are assumed to occur along only triple junctions.

Let us assume that diffusion coefficient is log-normally distributed in a nanocrystalline specimen. That is, its distribution is given as:

$$\rho(D) = \frac{1}{D\sqrt{2\pi s^2}} \exp\left(-\frac{(\ln D - \overline{\ln D})^2}{2s^2} \right), \qquad (1)$$

where $\overline{\ln D}$ and s are the mean value and standard deviation of $\ln D$, respectively.

In general, diffusion is a non-stationary process whose rate is characterized by experimentally measured penetration depth of diffusing species. In this context, the effective diffusion coefficient (that specifies the penetration depth during some time interval) can be defined only at concrete initial and boundary conditions. In the framework of our model, we will consider diffusion along triple junction lines of a two-dimensional solid with a square network formed by these triple junction lines (Fig. 1). The concentration of diffusing atoms at the boundary (x=0) of the solid is assumed to be constant: $c(x=0)=c_0$. (In doing so, the concentration is defined as the ratio of the number of crystal lattice sites occupied by diffusing atoms to that of host atoms.) The square network of triple junction lines is characterized in our calculations by a finite length and width. That is, coordinates (x,y) of points belonging to the finite

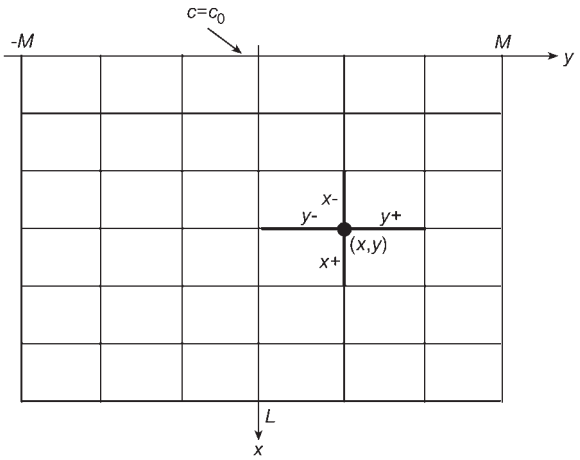


Fig. 1. A square network of triple junctions (a model of triple junction ensemble in a nanocrystalline solid).

rectangular box (simulation box) occupied by the network obey the following conditions: $0<x<L$, $-M<y<M$. In these circumstances, we assume the periodic boundary conditions, $c(y=-M)=c(y=M)$ and $j_y(y=-M)=j_y(y=M)$, to be realized at the boundaries $y=\pm M$. Here j_y is the projection of the flux $\boldsymbol{j}$ of diffusing atoms onto the axis y, which is in the following relationship with the concentration c and diffusion coefficient D: $\boldsymbol{j}(x,y)=-D(x,y)\nabla c(x,y)$. Also, for definiteness, we assume that the boundary $x=L$ is a reflecting one: $j_x(x=L)=0$. With relationship $j_x=-D\,\partial c/\partial x$, the above boundary condition at $x=L$ means that $\partial c/\partial x\,(x=L)=0$. For aims of this paper focused on calculation of the effective diffusion coefficient which takes into account the distribution of diffusivities along triple junctions, we will consider diffusion processes in the situation where the effect of the reflecting boundary $x=L$ (which hampers diffusion) is small. It is the case of low concentration of diffusing atoms at the reflecting boundary: $c(x=L,y)<10^{-3}\,c_0$ at any y.

The equation of diffusion along the triple junction line serving as a one-dimensional diffusion channel is as follows [26]:

$$\frac{\partial c}{\partial t} = D_i \frac{\partial^2 c}{\partial q^2}. \qquad (2)$$

Here i and D_i are the number and diffusion coefficient of a triple junction, respectively; $q=x$ and $q=y$, if the triple junction is parallel with axis x and y, respectively. Eq. (2) describes diffusion along one triple junction with a constant diffusion coefficient. However, this equation does not allow one to calcu-

Fig. 2. Two triple junctions joined at node point $y=0$.

late the concentration c of diffusing atoms at quadruple nodes of the triple junction network, where triple junction lines intersect.

In order to calculate c in the nodes in question, first, let us consider the simplified situation with two triple junctions, 1 and 2, that join at (double) node point with $y=0$ (Fig. 2). Let the triple junction 1 (2, respectively) occupy the region $-l<y<0$ ($-l<y<l$, respectively). The energy of vacancy migration from the node point $y=0$ to the triple junctions 1 and 2 is tentatively equal to E_{m1} and E_{m2}, respectively. The energy of vacancy formation in the triple junctions 1 and 2 is tentatively equal to E_{f1} and E_{f2}, respectively. These energies characterize triple junction diffusion. Actually, the probability of jump of an atom from the node to the triple junction i (i=1,2) is $\gamma_i=\gamma_0 \exp[-(E_{mi}+E_{fi})/(kT)]$, where k is the Boltzmann constant, and T is the absolute temperature. In these circumstances, the probability of a jump of an atom (an elementary act of vacancy migration) from the node $y=0$ to the triple junction i (and vice versa) is equal to the probability of an atomic jump in the junction line i. This probability (or, in other terms, frequency of atomic jumps), in its turn, can be expressed through the diffusion coefficient D_i that characterizes the triple junction i: $D_i=\gamma_i/a^2$, where a is the mean interatomic distance in the triple junction phase.

Now let us turn to the discussion of diffusion processes occurring via atomic jumps at quadruple node points formed by triple junctions. Let (x, y) be the quadruple node where the four triple junctions intersect which are denoted as $x+$, $x-$, $y+$, and $y-$ junctions (Fig. 1). The probability (frequency) ν_1 of atomic jumps from point (x, y) to the adjacent triple junctions is

$$\nu_1(x,y) = (\gamma_{x+} + \gamma_{x-} + \gamma_{y+} + \gamma_{y-})c(x,y). \qquad (3)$$

Here $c(x,y)$ is the relative concentration of diffusing atoms in point (x, y) (it is equal to the probability of location of a diffusing atom at this point), γ_{x+}, γ_{x-}, γ_{y+} and γ_{y-} are the probabilities of atomic jumps from point (x,y) to the triple junctions $x+$, $x-$, $y+$, and $y-$, respectively.

The probability ν_2 of atomic jumps from the adjacent triple junctions to point (x, y) is as follows:

$$\nu_2(x,y) = \gamma_{x+}c(x+a,y) + \gamma_{x-}c(x-a,y) + \gamma_{y+}c(x,y+a) + \gamma_{y-}c(x,y-a), \quad (4)$$

where a is the mean interatomic distance in the triple junctions phase. In these circumstances, a change of the relative concentration per unit time is equal to the difference $\nu_2 - \nu_1$ follows as

$$\frac{\partial c(x,y)}{\partial t} = (D_{x+}[c(x+a,y) - c(x,y)] + D_{x-}[c(x-a,y) - c(x,y)] + D_{y+}[c(x,y+a) - c(x,y)] + D_{y-}[c(x,y-a) - c(x,y)]) / a^2. \quad (5)$$

In formula (5), we have used diffusion coefficients D_{x+}, D_{x-}, D_{y+}, and D_{y-} which are in the following relationships with the corresponding probabilities of atomic jumps in the triple junction tubes $x+$, $x-$, $y+$, and $y-$, respectively: $D_{x\pm}=\gamma_{x\pm}/a^2$, $D_{y\pm}=\gamma_{y\pm}/a^2$.

In the situation where atoms are located at boundaries of the triple junction network, that is, at $y=\pm M$, formula (5) is modified in order to take into account the boundary conditions. In doing so, in particular, atoms from points (x, M) and $(x, 0)$ are assumed to be able of jumping to points (x, a) and $(x, M-a)$, respectively. In other words, with the boundary conditions discussed, the square network of triple junctions has the geometry of a cylinder.

3. DEFINITION OF EFFECTIVE DIFFUSION COEFFICIENT OF TRIPLE JUNCTION NETWORK

In order to calculate the diffusion rate along triple junctions forming the square network (Fig. 1), first, let us consider a simplified situation where diffusion coefficients of all 'horizontal' triple junctions (parallel with the axis y) are equal to 0, and diffusion coefficients of all 'vertical' triple junctions (parallel with the axis x) are identical and equal to D. In this situation, diffusion occurs only along the axis x, and a description of diffusion processes occurring in the square network of triple junctions is reduced to the well-known problem of one-dimensional diffusion described by equation:

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2}, \quad x > 0,\ t > 0, \quad (6)$$

with the boundary condition $c(x=0)=c_0$ and the initial condition $c(t=0)=0$. Analytic solution of this one-dimensional equation is given as [26]:

$$c(x,t) = c_0\left(1 - \mathrm{erf}\frac{x}{2\sqrt{Dt}}\right), \quad (7)$$

where $erf(u) = (2/\sqrt{\pi})\int_0^u \exp(-t^2)dt$ is the error function. With formula (7), one easily finds the mean value of $\overline{x^2}$, where x is the penetration depth of diffusing atoms, to be given as:

$$x^2 = \frac{\int_0^\infty x^2 c(x,t)dx}{\int_0^\infty c(x,t)dx} = \frac{4}{3}Dt. \quad (8)$$

From formula (8) it follows that $D=3\overline{x^2}/(4t)$.

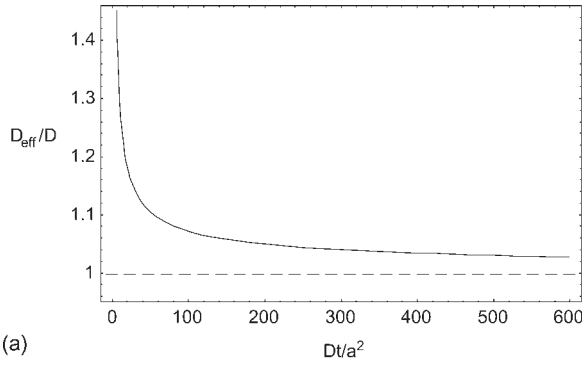
Now let us consider the situation where values of diffusion coefficient are log-normally distributed over triple junctions that form the square network (Fig. 1). With diffusion rate characterized by the penetration depth of diffusing atoms, by analogy with the one-dimensional diffusion discussed previously, we define the effective diffusion coefficient D_{eff} as

$$D_{eff} = \frac{3}{4}\frac{x^2}{t}. \quad (9)$$

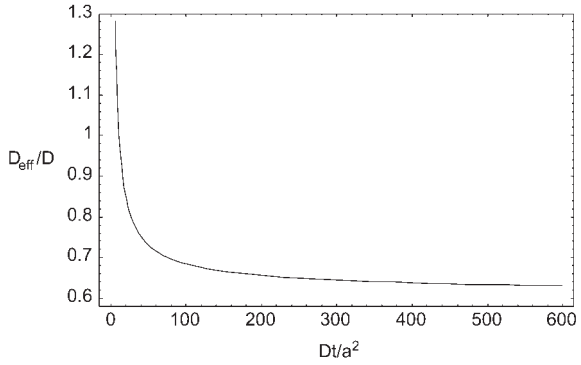
In the partial case of one-dimensional diffusion characterized by coefficients D along vertical triple junctions (see above), from definition (9) we have $D_{eff}=D$.

4. NUMERICAL CALCULATION OF EFFECTIVE DIFFUSION COEFFICIENT OF TWO-DIMENSIONAL TRIPLE JUNCTION NETWORK

We have numerically integrated diffusion Eqs. (2) and (5) at given initial and boundary conditions (see section 2), for various triple junction $m\times n$ networks. The number m of vertical triple junctions ranges from 25 to 40, while the number of horizontal triple junctions is chosen as $n=5$. Diffusion coefficients of triple junctions whose values are log-normally distributed by formula (1) with given $\ln\overline{D}$ and different values of s, are determined with the help of the generator of random numbers. The number m of horizontal triple junctions (parallel with the axis x) is chosen in such a way as to provide both the condition that $c(x=L) < 10^{-3} c_0$ and a sufficient accuracy of calculations of the effective diffusion coefficient D_{eff}. In the proce-



(a)



(b)

Fig. 3. Dependences of effective diffusion coefficient (calculated values) on Dt/a^2 in (a) triple junction network consisting of vertical junctions with identical diffusion coefficients D ($\neq 0$) and horizontal junctions with diffusion coefficients =0; and (b) triple junction network consisting of vertical and horizontal junctions with identical diffusion coefficients D. (Horizontal dashed line in Fig. 3a corresponds to value of D_{eff}/D, obtained in the framework of the continuum diffusion model; see formulas (7) and (8)).

dure of integration of Eqs. (2) and (5), triple junctions have been divided into segments of small length.

The numerical integration of diffusion Eqs. (2) and (5) is an iteration process in which a change of the concentration at any iteration step is calculated using the value of the concentration calculated at the preceding step. Periodically (after a certain number of the iteration steps) we have calculated the effective diffusion coefficient, using the calculated values of the concentration. It is worth noting that even in the case of the one-dimensional diffusion (discussed in section 3) the numerical integration provides only gradual approaching of the calculated value of D (Fig. 3a). It is related to a discrete character of our model. A similar gradual approaching of the numerically calculated D_{eff} to its real values is realized in the case of the triple junction network with all, vertical and horizontal, triple junctions having the same diffusivity D (Fig. 3b).

In the case of the triple junction network with log-normally distributed diffusivities, we have another peculiarity of the numerical calculation scheme in addition to the gradual approaching of D_{eff} to its limiting value. More precisely, in our calculations, value of D_{eff} fluctuates due to finite dimensions of the triple junction network. For instance, fluctuations of D_{eff} come into play when many atoms diffuse along one triple junction of the junction network, which has diffusivity essentially exceeding the mean diffusivity of triple junctions forming the network.

The limiting values of $D_{eff}/\overline{D}$ (where $\overline{D}$ is the mean diffusion coefficient of triple junctions composing the network shown in Fig. 1) at $t \to \infty$ are estimated with the help of curves $D_{\text{eff}}(t)$ at different values of parameter s. For any value of s, the generator of random numbers produces several distributions of diffusion coefficient values.

Then values of D_{eff}, calculated with these distributions, are averaged. The results of such calculations are presented in Table 1. We have not calculated D_{eff} in the case of s=2, because of very low convergence of the calculated values of D_{eff} to their limiting values.

The calculated values of D_{eff}, for various s, can be approximated by the following function:

$$D_{eff} = 0.6\overline{D}b^{-s^r}, \qquad (10)$$

where b and r are coefficients of the approximation. Finding the logarithm of (10) yields: $\ln(0.6\overline{D}/D_{eff}) = s^r \ln b$. Finding the logarithm of this expression gives: $\ln\ln(0.6\overline{D}/D_{eff}) = \ln\ln b + r\ln s$. Thus, if the dependence $D_{eff}(s)$ is well approximated by function (10), the dependence of $\ln\ln(0.6\overline{D}/D_{eff})$ on $\ln s$ should be a straight line. As follows from Fig. 4, points ($\ln s$, $\ln\ln(0.6\overline{D}/D_{eff})$) that correspond to numerically calculated values of D_{eff} at various s (see Table 1) are very close to the interpolation line. The coefficients r and b are determined from respectively the slope angle of the interpolation line and values of $\ln\ln(0.6\overline{D}/D_{eff})$ at $\ln s$=0. In doing so, we have: $r \approx 1.79$, and $b \approx 1.77$.

Thus, according to results of our theoretical analysis, the effective diffusion coefficient D_{eff} (taking into account diffusion percolation along triple junctions) is essentially different from the mean diffusion coefficient $\overline{D}$. The ratio $D_{eff}/\overline{D}$ is always <1. It rapidly

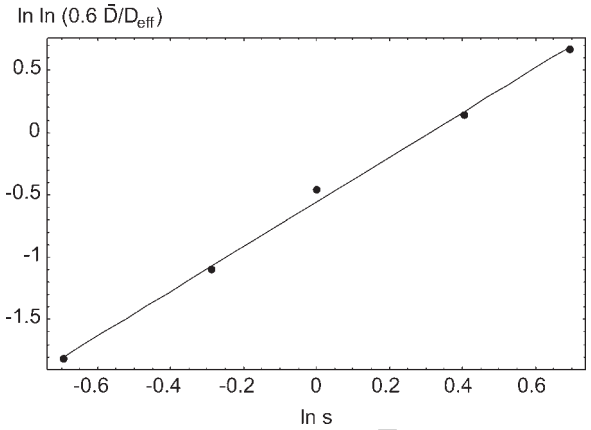


Fig. 4. Dependence of $\ln \ln(0.6\overline{D}/D_{eff})$ on $\ln s$: numerically calculated values (circles) and interpolation line.

decreases with the broadening of the distribution in diffusivities along triple junctions composing a triple junction network in a nanocrystalline solid.

5. CONCLUDING REMARKS

In this paper, diffusion percolation along networks of triple junction tubes in nanocrystalline materials has been theoretically described. In the framework of the suggested model description, triple junctions that form a network in a nanocystalline specimen are characterized by different values of diffusion coefficient. In these circumstances, the triple junction network is specified by both its geometry and a diffusion coefficient distribution among its elements, triple junction tubes. The effective diffusion coefficient D_{eff} is calculated which takes into account both these factors, geometry and distribution. In calculation of D_{eff}, we have used the solution of the problem of atomic diffusion from the free surface of a semi-infinite solid. According to our numerical calculations, the effective diffusion coefficient D_{eff} is always lower than the average diffusion coefficient $\overline{D}$ and highly sensitive to parameter s characterizing the width of the diffusion coefficient distribution. More precisely, ratio $D_{eff}/\overline{D}$ (<1) rapidly decreases with rising parameter s, that is, with the broadening of the distribution in diffusivities along triple junctions in a nanocrystalline solid. This tendency reflects the fact that diffusivity of a triple junction network is more influenced by contributions of its structural elements – triple junction tubes – with a low diffusivity, compared to those of triple junction tubes with a high diffusivity. These results should be taken into account in an adequate description of enhanced

Table 1. Values of effective diffusion coefficient D_{eff}.

s	0	0.5	0.75	1	1.5
$D_{eff}/\overline{D}$	0.60	0.51	0.43	0.32	0.24
s	2				
$D_{eff}/\overline{D}$	0.085				

sensing and mechanical properties of nano-crystalline materials with very small grains, since these properties strongly depend on triple junction diffusion processes. Also, the methods of the theoretical and numerical analysis of triple junction diffusion in single-phase nanocrystalline materials, developed in this paper, can be effectively extended to a description of diffusion processes in nanocomposite materials and nanomaterials with a bimodal structure consisting of a nanocrystalline matrix with embedded microscale grains.

ACKNOWLEDGEMENTS

This work was supported, in part, by the Office of US Naval Research (grant N00014-01-1-1020), INTAS (grant 03-51-3779), Russian Science Support Foundation, Russian Fund of Basic Research, Russian Academy of Sciences Program 'Structural Mechanics of Materials and Construction Elements', St. Petersburg Scientific Center, and 'Integration' Program (grant B0026).

REFERENCES

[1] H. Gleiter // *Acta Mater.* **48** (2000) 1.
[2] *Nanomaterials for Structural Applications*, *MRS Symp.Proc*., Vol. 740, ed. by C.C. Berndt, T. Fischer, I.A. Ovid'ko, G. Skandan and T. Tsakalakos (MRS, Warrendale, 2003).
[3] *Nanotechnology Research Directions*, ed. by M.C. Roco, R.S. Williams and P. Alivisatos (Kluwer, Dordrecht, 2000).
[4] *Nanoclusters and Nanocrystals*, ed. by H.S. Nalwa (American Sci. Publ., California, 2003).
[5] A.H. King // *Interf. Sci.* **7** (1999) 251.
[6] G. Palumbo and K.T. Aust // *Mater. Sci. Eng. A* **113** (1989) 139.
[7] K.M. Yin, A.H. King, T.E. Hsieh, F.R. Chen, J.J. Kai and L. Chang // *Microscopy and Microanalysis* **3** (1997) 417.
[8] B. Bokstein, V. Ivanov, O. Oreshina, A. Peteline and S. Peteline // *Mater. Sci. Eng. A* **302** (2001) 151.

[9] M.Yu. Gutkin and I.A. Ovid'ko // *Philos. Mag. A* **70** (1994) 561.
[10] H. Hahn and K.A. Padmanabhan // *Philos. Mag. B* **76** (1997) 559.
[11] D.A. Kostantinidis and E.C. Aifantis // *Nanostruct. Mater*. **10** (1998) 1111.
[12] A.A. Fedorov, M.Yu. Gutkin and I.A. Ovid'ko // *Acta Mater.* **51** (2003) 887.
[13] E. Owusu-Boahen and A.H. King // *Acta Mater*. **49** (2001) 237.
[14] M.Yu. Gutkin, I.A. Ovid'ko and N.V. Skiba // *Acta Mater.* **51** (2003) 4059.
[15] A.A. Fedorov M.Yu. Gutkin and I.A. Ovid'ko // *Scripta Mater.* **47** (2002) 51.
[16] G. Gottstein, A.H. King and L.S. Shvindlerman // *Acta Mater.* **48** (2000) 397.
[17] L.S. Shvindlerman and G. Gottstein // *Mater. Sci. Eng. A* **302** (2001) 141.
[18] K.S. Kumar, S. Suresh, M.F. Chisholm, J.A. Horton and P. Wang // *Acta Mater.* **51** (2003) 387.
[19] I.A. Ovid'ko and A.G. Sheinerman // *Acta Mater.* **52** (2004) 1201.
[20] A.P. Sutton and R.W. Balluffi, *Interfaces in Crystalline Materials* (Oxford Science Publ., Oxford, 1995).
[21] H.S. Kim, Y. Estrin and M.B. Bush // *Acta Mater.* **48** (2000) 493.
[22] S. Verpek and A.S. Argon // *J. Vac. Sci. Technol.* **20** (2002) 650.
[23] S. Verpek // *Rev. Adv. Mater. Sci.* **5** (2003) 6.
[24] *Mechanical Properties of Nanostructured Materials and Nanocomposites*, *MRS Symp. Proc., Vol. 791*, ed. by I.A. Ovid'ko, C.S. Pande, R. Krishnamoorti, E. Lavernia and G. Skandan (MRS, Warrendale, 2004).
[25] M.Yu. Gutkin and I.A. Ovid'ko, *Plastic Deformation in Nanocrystalline Materials* (Springer, Berlin/New York, 2004).
[26] B.S. Bokstein, *Diffusion in Metals* (Metallurgiya, Moscow, 1978), in Russian.